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### (54) TOOTH RESTORATION COMPOSITION, STRUCTURE AND METHODS.

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**Description**Technical Field

5 This invention has to do with compositions, structures and method for the restoration of natural teeth by application of permanent fillings, crowns, replacements, adhesion of like or dissimilar restorative materials such as amalgam and acrylate resin based restoratives, all based on the discovery of a remarkable urethane polymer system which for the first time enables posterior reconstructions of natural teeth having a toughness as opposed to mere hardness so as to reversibly thermodynamically absorb and return occlusal stresses encountered in mastication, avoiding creep and like maleffects common in other resinous tooth restoratives such as acrylate resins. More particularly, the invention is concerned with methods of forming especially in situ within broad and forgiving clinical parameters a tooth restorative composite which obsoletes previously known resinous restoratives by being readily initially formed in situ during a precure period, e.g. by being syringeable into the prepared tooth, condensible on site, adherent to tooth walls, 15 including margin areas, nonadherent to instruments, and easily trimmed for a reasonable period after initial cure, all while affording the uniquely advantageous final properties noted above.

Background Of The Invention

20 Amalgams of silver have long been used in tooth restorations, but they contain mercury and may constitute a health hazard and they are expensive and not esthetic. Moreover, because they are not adherent to the tooth, extra large and undercut preparations in the tooth are required, leaving less of the tooth than might be desirable merely to remove carious conditions.

Acrylate resins have found a market particularly where esthetics are important, e.g. repair of anterior teeth. Transfer of acrylate resins to posterior teeth has been largely unsuccessful, since acrylates are glassy polymers at the temperature of the mouth environment, and as such tend to creep under stress and ultimately fail structurally. In addition, application of acrylate resins is fraught with difficulty, including adhesion of the acrylate to the instruments but not to the tooth structure, causing leakage at the restoration margins, inability to syringe the material into the cavity, inability to condense the positioned resin, hardness 30 without toughness in the cured resin, and hydrophobicity alien to natural structures.

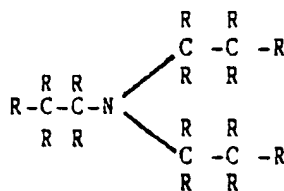
Summary Of The Invention

It is accordingly an object of the invention to provide a novel restorative tooth composition, structure and method. Another object is to provide such a composite wherein natural tooth color is closely matched, 35 the cured resin is indestructible once cured, the morphological structure of the resin is such that the structure is phase segregated into crystalline and amorphous zones defining a truly thermodynamic polymer capable of receiving work energy, delocalizing it and returning it to its surroundings after each mastication cycle so as to avoid destruction inherent in retaining such energy. It is another object to provide such resin which is not clinically critical because its progression is gradual, predictable, and reproducible, because it tolerates mismatching of quantities of reactants, is mixable as a pair of pastes, is so fluid that it can be syringed into place, is non adhesive to dental instruments, requires minimum removal of the natural tooth since it is fluid and self-adheres to the tooth surfaces upon cure, edge margin seals against leakage, can be condensed for perfect interfitment with the tooth preparation, can be swaged and carved to form the 45 approximate occlusal anatomy, and any excess wiped or trimmed away, minimizing grinding time, is low exothermic minimizing injury to tissue, is nonconductive to heat and cold insofar as pulpal response is concerned, equals or exceeds in abrasion resistance silver amalgam, is less stain prone than acrylates, is easily veneered in successive layers increasing clinical options even at widely spaced time periods by virtue of its adhesive and cohesive properties, accepts large quantities of fillers such as vitreous particulate, 50 but does not depend on such for effective performance in a tooth, is free of immune sensitization, oral toxicity, cyto-toxicity and mutagenicity by common tests, is radiopaque, and which, in sum, offers a combination of chemical, clinical and performance attributes which make it the material of choice for all dental restorations hereinafter done.

These and other objects to become apparent hereinafter are realized in accordance with the invention 55 by the method of forming a composition useful for restorative tooth structures, including mixing a first side comprising an isocyanato reagent under urethane polymer forming conditions simultaneously with a second side comprising a premix of an hydroxylated tertiary amine reagent and a polyol reagent, shaping for use in a tooth restoration, and reacting to form a polymeric urethane composition useful for restorative tooth

structure.

In this and like embodiments, there is included also selecting an isocyanato reagent comprising 4,4'-diphenylmethanediisocyanate; cyclizing the 4,4'-diphenylmethane diisocyanate with itself before mixing for urethane polymer forming reaction; dissolving the cyclized 4,4'-diphenylmethane diisocyanate in non-cyclized 4,4'-diphenylmethane diisocyanate before mixing under urethane polymer forming conditions; selecting an isocyanato reagent comprising the polyfunctional isocyanate addition reaction product of an aromatic polyfunctional isocyanate moiety and a hydrophobic organic polyfunctional active hydrogen moiety, e.g. selecting 4,4'-diphenylmethane diisocyanate as the aromatic polyfunctional isocyanate moiety, cyclizing the 4,4'-diphenylmethane diisocyanate and dissolving it in a solution of 4,4'-diphenylmethane diisocyanate in advance of the addition reaction, selecting Isonate<sup>®</sup>143-L or Mondur<sup>®</sup> CD as the aromatic polyfunctional isocyanate moiety, and selecting hydroxyl-, thiol-, or carboxyl- poly-substituted compounds reactive with isocyanate groups as the hydrophobic organic polyfunctional active hydrogen moiety; selecting polytetraalkyleneoxide ether polyols, polyoxyalkyleneoxide ether polyols, aliphatic diols, or active-hydrogen substituted oligomers and fatty acid esters reactive with isocyanate groups as the hydrophobic organic polyfunctional active hydrogen moiety; selecting active hydrogen substituted silicone, fluorocarbon, fluorochlorocarbon, polytetraalkyleneoxide ether polyols, acrylic, vinyl, butadiene, cis-polyisoprene, polyamide, polyester, vinyl acetate, acrylamide, polyolefin, or Diels-Alder adducts of unsaturated polyester resin oligomers as the hydrophobic organic polyfunctional active hydrogen moiety; also selecting polytetramethyleneoxide ether polyol, D.B. castor oil, or hydroxylated glyceryltriricinoleate triester reactive with isocyanate as the hydrophobic organic polyfunctional active hydrogen moiety; reacting the 4,4'-diphenylmethane diisocyanate and the hydroxylated glyceryltriricinoleate triester or like reagent in an inert vessel under high shear conditions at a temperature of about 80°C. for about one hour under a vacuum in excess of 1.3 mbar (one millimeter of mercury); effecting the reaction to an amine equivalency in the product of above about 400; selecting as the polyol reagent a polyol forming a noncrystalline urethane polymer with the isocyanato reagent under urethane polymer forming conditions; as the polyol an hydroxyl-, thiol-, or carboxyl- poly-substituted oligomer having a molecular weight above about 500 and segregated phase defining reaction with the isocyanato reagent relative to said amine reaction under the same urethane polymer forming conditions; selecting a polyoxyalkylene ether polyol as the polyol reagent; selecting a polyoxyalkylene ether polyol having a molecular weight above about 1000; reacting the polyol with an isocyanato reagent comprising an adduct of liquid 4,4'-diphenylmethanediisocyanate and glyceryltriricinoleate triester to form a noncrystalline urethane polymer; reacting the polyol and isocyanato reagent adduct in admixture with a tertiary amine having a faster rate of reaction with the isocyanato reagent adduct than does the polyol; selecting as the hydroxylated tertiary amine reagent an alkaryl amine, arylamine, mercaptan, alkylene oxide adduct of alkanol amines, alkoxylated or epoxylated ethylenediamines, triazines, amines and hydrazines having hydroxyl, thiol, or carboxyl functionality; selecting as the hydroxylated tertiary amine reagent a compound having the formula:



in which at least one R = R<sub>1</sub>, and each remaining R is R<sub>1</sub> or R<sub>2</sub>, and:

in which:

- R<sub>1</sub> = -OH; -SH; -N(CH<sub>2</sub>CH<sub>2</sub>)OH<sub>2</sub>;  
 -N(CH<sub>2</sub>CH<sub>3</sub>CH<sub>2</sub>OH)<sub>2</sub>; -N(CH<sub>2</sub>CHCH<sub>3</sub>OH)<sub>2</sub>.  
 R<sub>2</sub> = -H; -Me; -Alkyl; -OAlk; -OMe; Halogen,

-Aryl;

-Aroyl

- selecting as the hydroxylated tertiary amine reagent the compound N,N',N',N'-tetrakis(2-hydroxypropyl) ethylenediamine; selecting as the isocyanato reagent 4,4'-diphenylmethane diisocyanate, and as the polyol reagent polyoxypropylene polyol triol; reacting the isocyanato reagent with the hydroxylated tertiary amine

<sup>®</sup>trademark

reagent to a crystalline urethane polymer, and with the polyol reagent to an amorphous polymer interdispersed with the crystalline polymer; employing as the first side per 100 parts by weight from 25 to 45 parts of 4,4'-diphenylmethane diisocyanate, from 3 to 8 parts of hydroxylated tertiary amine, glyceryltricinoleate triester or polytetramethyleneoxide ether polyol adducted with the 4,4'-diphenylmethane diisocyanate, and the balance a hardening filler; and employing as the second side per 100 parts by weight from 10 to 30 parts of the polyol, from 10 to 30 parts of the hydroxylated tertiary amine, and the balance zeolite, silica, including silane treated silica, vitreous particulate or mixtures thereof.

The invention further contemplates compositions and structures including the composition useful for restorative tooth structures, comprising a urethane polymer reaction product in the shape of a tooth restoration structure of a first side comprising an isocyanato reagent reacted simultaneously with a second side comprising a premix of an hydroxylated tertiary amine reagent and a polyol reagent.

In this and like embodiments, isocyanato reagent typically comprises 4,4'-diphenylmethanediisocyanate. the isocyanato reagent comprises cyclized 4,4'-diphenylmethane diisocyanate; the isocyanato reagent comprises the cyclized 4,4'-diphenylmethane diisocyanate dissolved in noncyclized 4,4'-diphenylmethane diisocyanate; the isocyanato reagent comprises the polyfunctional isocyanate addition reaction product of an aromatic polyfunctional isocyanate moiety and a hydrophobic organic polyfunctional active hydrogen moiety; the aromatic polyfunctional isocyanate moiety comprises 4,4'-diphenylmethane diisocyanate; the 4,4'-diphenylmethane diisocyanate is cyclized and dissolved in a solution of 4,4'-diphenylmethane diisocyanate; the moiety is Isonate<sup>®</sup> 143-L or Mondur<sup>®</sup>CD; the hydrophobic organic polyfunctional active hydrogen moiety comprises hydroxyl-, thiol-, or carboxyl- poly-substituted compounds reactive with isocyanate groups; the hydrophobic organic polyfunctional active hydrogen moiety comprises polyoxyalkyleneoxide ether polyols, aliphatic diols, or active-hydrogen substituted oligomers and fatty acid esters reactive with isocyanate groups; the hydrophobic organic polyfunctional active hydrogen moiety comprises active hydrogen substituted oligomers selected from silicone, fluorocarbon, fluorochlorocarbon, acrylic, vinyl, butadiene, cis-polyisoprene, polyamide, polyester, vinyl acetate, acrylamide, polyolefin, or Diels-Alder adducts of unsaturated polyester resin oligomers; the hydrophobic organic polyfunctional active hydrogen moiety comprises hydroxylated glyceryltricinoleate triester reactive with isocyanate; the 4,4'-diphenylmethane diisocyanate and the hydroxylated glyceryltricinoleate triester compounds are prereacted in a chemically inert vessel under high shear conditions at a temperature of about 80°C. for about one hour under a vacuum in excess of 1.3mbar (one millimeter of mercury); the prereacted compounds have an amine equivalency in the product of above about 400; the polyol reagent is a polyol preferentially forming a noncrystalline urethane polymer with the isocyanato reagent under urethane polymer forming conditions; the polyol is an hydroxyl-, thiol-, or carboxylpoly-substituted oligomer having a molecular weight above about 500 and a segregated phase defining reaction with the isocyanato reagent than the amine reaction with the isocyanato reagent under the same urethane polymer forming conditions; the polyol reagent is a polytetraalkyleneoxide ether polyol or polyoxyalkylene ether polyol; the polyol has a molecular weight above about 1000; the urethane polymer is obtained by reaction of the polyol with an isocyanato reagent comprising an adduct of liquid 4,4'-diphenylmethanediisocyanate and polytetramethyleneoxide ether polyol, D.B. castor oil, or glyceryltricinoleate triester and is a noncrystalline urethane polymer; tertiary amine reagent has a faster rate of reaction with the isocyanato reagent adduct than does the polyol reagent, whereby the urethane polymer comprises a crystalline portion produced by reaction of the amine and the adduct and a noncrystalline portion produced by reaction of the polyol and the adduct, the crystalline portion being dispersed through the noncrystalline portion; the hydroxylated tertiary amine reagent comprises an alkylene oxide adduct of alkanol amines, alkoxylated or epoxylated ethylenediamines, triazines, amines and hydrazines having hydroxyl, thiol, or carboxyl functionality.

#### Preferred Modes

The ensuing detailed description of a preferred embodiment of the invention tooth restorative, its precursors and products has reference to the properties of the components during their various stages toward achieving the final composite state: during (1) storage of Part A (sometimes first part or side) and Part B (sometimes second part or side) in their respective containers; (2) the initial mixture of the components; (3) the malleable phase; (4) the final composite state.

In preparation, the first step is the synthesis of the Part A and Part B components. For the Part A component: 4,4'-diphenylmethane diisocyanate (sometimes MDI) is converted through the Wittig reaction into a cyclized form which is then dissolved in a solution of MDI to produce a storage-stable liquid form

\* registered trademark

called liquid MDI having an overall isocyanate functionality of 2.1 to 2.2. Pure 4,4'-diphenylmethane diisocyanate could have been selected to produce the prepolymer, but this special form was used as the reactive isocyanate in order to produce a more storage-stable solution (stable towards freezing during storage). This liquid MDI form is commercially available from Upjohn Company as Isonate<sup>®</sup>143-L or from

5 Mobay Chemical as Mondur<sup>®</sup> CD.

A quasi prepolymer is synthesized from the addition reaction of liquid MDI (Mondur<sup>®</sup> CD) and preferably glyceryltriricinoleate triester (sometimes GTR). Placed into the reaction solution was Kimble T-3000 ground barium borosilicate glass of a nominal 10 $\mu$ m (micron) diameter particle size along with fumed silica of a 0.04 $\mu$ m (micron) size. This composition was placed in an inert reaction vessel which was capable of heating the reaction mixture, controlling its reaction temperature, high-shear mixing, and a vacuum exceeding one millimeter. The ingredients were high-shear mixed and heated to 80-85 degrees centigrade for one hour. During this time, a vacuum was pulled on the mixture in excess of 13mbar (one millimeter of mercury). The amine equivalent was measured and the synthesized mixture packaged in metal squeeze tube containers which acted as a non-permeable barrier to moisture. The ratio of the ingredients is such that the overall theoretical amine equivalent weight of the prepolymer mixture was 451.5. The actual amine equivalent weights achieved ranged from 460 to 465. The barium borosilicate glass and fumed silica were selected from the available fillers for the following properties: providing a non-basic residual which would otherwise produce an unstable prepolymer mixture (tending to form isocyanurate reaction products), radioopaque properties, fineness of particle size and acceptable color and translucency. The barium borosilicate glass is unique in its regard to produce stable isocyanate prepolymers, presumeable because of the more strongly acidic (Lewis acid) borosilicate moiety in combination with the weakly basic barium moiety.

The Part A (prepolymer) component utilizes the extremely hydrophobic glyceryltriricinoleate triester hydroxyl-functional compound, a refined castor oil. This compound was selected on the basis that its hydrophobic character stabilized the prepolymer towards reaction with extraneous moisture contamination, during the following stages of its potential exposure to moisture: preparation of the prepolymer, packaging of the Part A component, storage of the Part A component in metal squeeze tube containers, mixing the Part A with the Part B component on the mix pad, introduction of the mixture to the oral cavity, residence of the polymerizing mixture in the prepared cavity and residence of the restoration in-vivo. Other hydroxyl-functional compounds which could have been selected to achieve this hydrophobic property include such compounds as polyoxytetramethyleneoxide ether polyols, polyoxypropylene ether polyols, cyclohexanediol, hexanediol, dipropylene glycol, tripropylene glycol, propylene glycol, ethylene glycol, diethyleneglycol, triethylene glycol, 1,3-butanediol, butanediol, propargyl alcohol, butyne diol, and the family of di- and tri-functional monomers or polyols, as well as silicone-, fluorocarbon-, fluorochlorocarbon-, acrylic-, vinyl-, butadiene-, cis-polyisoprene-, polyamide-, polyimide-, Diels-Alder adducts of unsaturated polyester resin-, polyester resins, vinyl acetate-, acrylamide-, polyolefin-, and any combination of the above oligomers modified to have active-hydrogen functionality. Carboxylic acid-functional-, thiol functional- and other active-hydrogen- functional oligomers or monomers can also be selected to be reacted with the isocyanate to form the prepolymer used as the isocyanate reagent.

The Part B (polyol reagent) is preferably partially composed of a high molecular weight polyol oligomer, e.g. a 2500 to 5000 up to 6000 molecular weight and higher liquid tri-functional polyoxypropylene ether polyol having some ethylene oxide capping to give secondary functionality. Any modification of the foregoing hydrophobic compounds may be selected as long as the reactivity of the polyol component is slower than the tertiary amine coreactant or such as to define a phase segregated polymer relative to that defined by the amine reaction with isocyanate during formation of the polymer, so that the polyol forms essentially (i.e. thermodynamically) random structure by virtue of having little ability to crystallize, or organize its structure, and it has the correct solubility to phase-segregate from the crystalline amine isocyanate adduct phase and to thereby form multi-phase matrix structures. In addition the polyol should have sufficient functionality to crosslink with the crystalline "zones" even if the clinician should mix the Part A and Part B components off-ratio enough to cause the cross-link density to be reduced, should have some tendency to cyclize or helixize, or form polymeric strands which are capable of being elongated when the multiphase structure is stressed by an outside force, and most importantly, have the ability to return to its random or amorphous structure once the external force, e.g. from mastication, is relieved.

In combination with the just-described polyol is a hydroxyl-reactive amine compound capable of forming highly crystallized and ordered structures upon reaction with the isocyanate functionality in the Part A component. The amine reagent preferably is a somewhat ordered structure containing tertiary amine groups. While not wishing to be bound to any particular theory of operation, it is theorized that the tertiary

\* registered trademark

amino groups of amine reagent herein, having a free-electron pair, orients that electron pair with some other moiety in the polymer solution (in its prepolymerized form) to resist unwanted melting during grinding in small less than one gram aliquots, whereby structures of adducts can be visualized which show a high crystalline and oriented structure capable of withstanding many kilocalories of input heat during a grinding process such as during the finishing of a restoration, and the highly organized nature of these crystalline zones can be supposed to have sufficient intramolecular forces to remain intact, while only amorphous zones would be unsupportive at their interstices and consequently "ablate" during the grinding process. In general it is significant that only the tertiary amino groups, not having reactive hydrogen functionality on the amino groups themselves in order to withstand instant reactivity, function herein as the amine reagent. In addition, the tertiary amino groups must have hydroxyl functionality adducted. The best means of adducting is to use ethylene oxide or propylene oxide so that only one ethylene or one propylene is adducted to each active hydrogen of the tertiary amino group. Illustrative amine reagents herein are: triethanol amine; tripropanol amine; combinations of diethanol-monopropanol amine, etc.; ethylenediamine tetra ethoxylate; ethylenediamine tetrapropoxylate; ethoxylated and propoxylated 1,3,5-triazines, or other triazine isomers; cyclic combinations of ethylenediamine, hydrazine, amines which are ethoxylated, propoxylated or epoxidized in any form which leaves hydroxyl, or thiol functionality.

The Part B side also contains a zeolite, such as a sodialuminosilicate zeolite structure, e.g. capable of containing at least one molecule of water within its clathrate structure. It has been found that levels of zeolite substantially exceeding 5 percent up to as much as 85% by weight substantially improve the malleable properties of the invention composition, and substantially improve the physical properties of the restorative for condensing, swaging, articulating, carving and grinding. Moreover, the invention composition is substantially improved in its resistance to side reactions with moisture, and maintains an "ablative" characteristic which is otherwise not present when this zeolite is not admixed. Again, it is theorized that the zeolite is acting synergistically with the amine reagent in producing the required "through-cure" and "ablative" properties so significantly present in the invention composition.

A radiopaque glass is also incorporated into the Part B side in certain preferred examples. This blend was prepared using the same reaction vessel described above. The ingredients were high-shear mixed in the vessel, heated to 105-110 °C in order to ensure that all water was removed from the mixture. The filled polyol component was packaged in its own separate metal squeeze tube container for storage.

The composition of the Part A and Part B pastes when extruded onto the mix pad, then upon being mixed and during the syringable stage is as follows: Both the Part A and Part B components desirably produce the correct viscosity pastes for extruding out of a number 10 orifice from a metal squeeze tube at nearly equal and controlled diameters. By extruding equal length lines of pastes on a moisture-resistant mixing pad, the volume ratios are maintained at roughly 1.00 to 1.00. The achievement of control of the mix ratios is very important for maintenance of the stoichiometry of the reactive components and for achieving maximum molecular weight polymers in the composite matrix. The composition is preferably built upon, e.g. the trifunctional ricinoleate, trifunctional high-molecular weight oligomer, and the tetra-functional N,N,N,N-tetrakis (2-hydroxyethyl or-propyl) ethylenediamine in order to achieve an extremely high level of off-ratio or poor mixing forgiveness encountered in lax clinical use of the product. The mixed ingredients have filler levels and matrix oligomer viscosities which are selected for being syringed into narrow-channeled cavities.

In the malleable phase, the Part A component, composed of 4,4'-diphenylmethane diisocyanate and 4,4'-diphenylmethane diisocyanate-glycerylricinoleate triester prepolymer, reacts first with the active hydrogen groups (hydroxyls) on the tertiary amine hard segment crosslinkers of the Part B component. The reaction of 4,4'-diphenylmethane diisocyanate is fast with the tertiary amine in comparison with the reactivities of the 4,4'-diphenylmethane diisocyanate prepolymers and the polyol reagent moieties. The fast reaction produces crystalline hard segments which align into morphological phases within the unreacted or partially-reacted polyol and 4,4'-diphenylmethane diisocyanate prepolymer phases. This crystalline composition within the liquid amorphous phases produces the malleable consistency of the mixture which occurs between two and four minutes after the start of mixing. Condensing the polymer at this point does not fracture the interstices because the amorphous phases have not yet cross linked with the crystalline phases. The forces of condensation merely cause laminar flow and alignment of the hard segments in the liquid soft segment medium. Polymerization continues until the soft segments crosslink the various hard segments and the polymer becomes intractable. At that point, the reversible thermodynamic feature of the invention is apparent as further deformation causes the polymer to uptake the external work of deformation and return it to the surroundings again when external deformation forces are relieved.

The fully-cured restorative is a multi-phase matrix where the crystalline zones (phases) of the matrix are contained within the amorphous zones. The crystalline zones are tied to the amorphous zones through the prepolymer portion of the Part A component. The multi-phase matrix has the capability of uptaking external

forces (e.g., from mastication) through thermodynamic ordering of the amorphous zones. The polyol has the capability or uptaking these stresses because the pendant methyl groups on the polyoxypropylene ether polyol provide barriers to rotation which can be easily overcome by the forces of deformation to produce a B-pleated sheet conformer if the need for uptaking work energy in the form of ordering (negative entropy) is required. Moreover, the pendant methyl groups provide only a low resistance to barriers of rotation allowing the number of possible structures to be high (high randomness) when external forces are relieved. This return of the work energy in the form of entropy prevents incipient destruction of the polymer by minimizing any retained work (low hysteresis).

It has been found that the invention compositions have natural adhesive affinity to conventionally etched enamel structure.

#### Clinical Properties

The paste-like components are easily extruded at equal lengths on a mix pad. The physical properties can depend upon the mix ratio accuracy and the mix intimacy between the Part A and Part B pastes. Tests have shown that level properties are maintained when the mix ratios have been purposely varied by approximately 2-times excess Part A and, conversely, 2-times excess Part B. In theory, the optimum properties are achieved when a 1:1 ratio by volume of Part A and Part B is used.

The components are mixed with a dental spatula and form a flowable paste composition. Back-filling into a syringe allows easy introduction into a prepared cavity. The viscosity is low enough that the composition can be introduced to the deepest portion of the cavity and injected as the syringe is drawn to the surface. It has been shown that nearly perfect adaption to the cavity walls is achieved. By comparison, acrylate composites are only difficultly placed into large cavity preparations mainly due to their pasty consistency and their inherent stickiness to placement instruments.

During the length of time typically required to complete this filling process, the mixture has achieved a consistency where it can be swaged to conform closely to the required anatomy. For example, a probe or similarly shaped instrument can be used to shape the occlusal anatomy for Class 1 restorations. This technique can reduce the grinding time typically required to achieve articulation.

The composition achieves the consistency of silver amalgam approximately four minutes after the start of mixing. This offers the additional convenience of allowing the composition to be condensed against the matrix band in Class 2 restorations. Nearly perfect interproximal adaptation can be achieved using this technique. This process also ensures marginal integrity and a perfect seal against invasive fluids and bacteria.

As noted above, during the process of condensing, the invention composition is not fractured, but it flows and knits with itself until further force from condensing will no longer create any flow or deformation. The composition adheres to etched enamel and dentin surfaces with each application of pressure from a plugging instrument. The plugging instrument neatly pulls away from the composite without stickiness. The polymerization reaction is gradual and predictable producing only a slight exotherm. The concomitant shrinkage at the bond line is almost insignificant and results in little or no residual stressing on the bond line after polymerization is complete. The limited shrinkage that does occur takes place on the non-contact surfaces.

Occlusal articulation can simply be achieved for Class 2 restorations using the following procedure: The prepared cavity is filled to a slight excess. After condensation, the patient then bites down on a thin plastic release film which causes the material to flow and to achieve the approximate occlusal anatomy. The excess flow has a hard rubber consistency and is easily trimmed off with a sharp-edged scraper or scalpel. Further grinding is not typically required but can be achieved with a fluted flame-tipped burr without galling. The composition properties allow a period for grinding from 6 to 20 minutes after the start of the procedure. Grinding does not cause shattering as can occur with acrylate composites.

The composition continues to harden at a controlled rate until nearly full properties are achieved after 2 hours. Full properties are achieved after 24 hours.

#### In-Vivo Properties

While long term testing results are not yet available, it is anticipated, because of the chemical nature and physical structure of the invention composition is likely to have substantial abrasion resistance in the mouth. Laboratory tests using accelerated methods show the composition to be superior to 3M's P10 acrylate glass composite and roughly equivalent to Phasealloy (trademark) amalgam. The elastomeric properties appear to provide resistance against marginal breakdown from the mechanical forces of

occlusion and from expansive and contractive forces from hot and cold liquids.

A considerable advantage of the present composition is that re-veneering is possible even after a long period from the first installation; the adhesion of the composition to itself allows this to be accomplished.

Restorations with the composition are non-toxic and have been tested for immune sensitization, oral toxicity, cyto toxicity and for mutagenicity (by the Ames Test). All results are negative. In addition the composition provides a resistance to thermal conductivity thus reducing pulpal sensitivity to hot and cold liquids, is esthetically attractive and nearly approximates the appearance of enamel in the posterior areas. It has less of a tendency to stain than acrylate composites.

## 10 Examples

### Example 1

Part A	
Mondur <sup>*</sup> CD	21.3
D.B. Castor Oil	3.6
Silaned Quartz	75.0

<sup>\*</sup> trademark

PART B	
6000 Mol Wt. Polyether Triol	18.0
N,N,N,N-tetrakis (2-hydroxypropyl) Ethylenediamine	9.0
Sodium Aluminosilicate Zeolite Powder	10.0
Silaned Quartz	57.8
Titanium Dioxide in Polyether Polyol, 50%	5.0
Dibutoxytin Disulfide	0.2

The composition reached a stage at approximately one minute after mixing when it was firm, non-tacky and easily placeable. It was condensible at this stage and gradually increased in hardness somewhat like amalgam so that continued compaction was achieved until 3-1/2 to 4 minutes when it was easily carvable and shapeable. After 5 minutes, it was at the hardness to be grindable. The hardness properties continued to build gradually to form a very hard elastomer after one hour when it reached nearly full properties. Full hardness properties were reached after 24 hours.

## 40 Control

3M's P10 restorative was a soft, gummy mixture for the first minute after the start of mixing. Between the period of one and 2-1/2 minutes the material was tacky and difficult to place. Placement could not be achieved with compaction except within the very narrow time-frame spanning approximately 5 seconds. During this 5 second period the resin gelled to form a weak soft composite. Compaction during and after gelation probably ran a high risk of fracturing the matrix. This evaluation is made on the basis that the material was weak and spongy just at the time of gelation until 30 seconds afterwards. Carving and grinding caused chipping when attempted within the first 2 minutes after gelation. The resin was hard but somewhat weak at this point.

To evaluate the invention composition, a second molar human tooth was ground flat on the occlusal surface. A circular cross-section was developed by grinding the mesial, distal, buccal and lingual surfaces to a diameter of 7.5 +/-0.5 mm. The ground tooth was then cast into a support block using a hard epoxy casting resin forming a cube which was 20 mm on each side. Then an aluminum block was machined into a cube having a face of 20 mm x 20 mm and being 10 mm thick. A hole was drilled through the face of the aluminum block having a diameter of 7 mm. By placing the aluminum block on top of the cast block containing the cast tooth, a test cavity was developed with the hole overlapping the exposed cementum surface. A jig was then designed to firmly hold the epoxy and aluminum blocks in the jaws of a tensile tester.



The cementum surface was then etched using 35% phosphoric acid for 120 seconds, washed clean with distilled water and blown dry using air. With the test cavity in place (out of the tester jaws), test material was mixed and compacted into the cavity using the clinical application and compaction procedures prescribed by the particular manufacturer. The bonded blocks were allowed to remain undisturbed for a period of 24 hours. The tensile mode of the tester was then used to measure the resistance to delamination of the interface between the cementum and the restorative material using a straining rate of 0.33 mm/sec. The results of the adhesion tests are shown in Table 1.

Table 1. Adhesion of Test Composite and Controls to Cementum:

<u>Test Material</u>	<u>Adhesion in the tensile mode, g/cm sq</u>
Phasealloy <sup>*</sup> amalgam	0
" "	0
P10 Composite, no post-gel compaction	70.3
P10 Composite, no post-gel compaction	421.8
P10 Composite, post-gel compaction	6467.
P10 Composite, post-gel compaction	1687.
Example I	7311.
Example I	5765.
* trademark	

P10 restorative was found to have highly variable bonding strengths depending upon the compaction technique. When compaction was accomplished prior to gelation, then the average of two duplicate tests was 211 g/cm sq. When compaction was continued during and after gelation, two duplicate tests gave average tensile strengths of 4077 g/cm sq. Our tests show that P10 acrylic composite has virtually no adhesion to etched-cementum without achieving compaction. The most obvious deficiency is that P10 (and all acrylics) resist being compacted due to an inherent lack of a continuous, non-accelerating build-up of hardness during polymerization.

Two duplicate tests were made using the Example I material. The urethane was mixed on the pad for 30 seconds, and a compaction instrument was used to deliver the urethane to the test cavity within 1 minute. Loading and compaction was continued until 3 minutes had elapsed. The composite was carved smooth after 5 minutes to simulate actual clinical methods. The composite was allowed to remain undisturbed for 4 hours before being tested. The average tensile strength was 6538 g/cm sq.

The Shore Durometer was used to determine the hardness of the Urethane and other materials. The results are shown in Table 2.

Table 2

Shore Durometer Hardness		
Sample Type	Shore D Hardness	
	Initial	10 second dwell
Example 1	91	90
	92	91
	93	92
	90	89
	89	87
P10 Acrylic composite	99	98
	98	98
	99	99
	98	98
	99	99
Amalgam	97	97
	99	98
	98	98
	97	97
	99	99
Human tooth enamel, 2nd molar exterior	100	100
	100	100
	100	100

Hardness has historically been considered one of the key parameters for judging the applicability of a prospective composite for posterior applications. Because enamel is the hardest of all naturally occurring biological materials, there apparently has been an a-priori requirement for occlusal restoratives to have enamel hardness in order to replicate the natural mastication processes. It is our feeling that a restorative material might not necessarily need to be as hard as enamel in order to provide mastication and have abrasion resistance. The invention composition has the hardness of a very hard elastomer, for all intents and purposes hard enough to resist most indentation forces.

#### Example 2

Example 1 was repeated using ground glass rather than quartz silica to improve color. The sample had a more natural tooth appearance.

Example 2			
Materials	Eq Wt	Eq	Weight
Mondur CD*, Mobay Chemical Co.	144	.244	35.2
DB Castor Oil, Caschem	315	.019	5.9
Corning 7740 Ground Glass	-	-	58.8
Total Part A	443	.225	99.9
Multranol* 3901	2000	.011	22.0
Quadrol*, BASF Wyandotte	73	.246	18.0
MS4A Powder	-	-	10.0
Corning* 7740 Ground Glass	-	-	50.0

\* trademark

The Example 2 composition was evaluated by a dentist. The product was introduced to him as a novel

composite. He evaluated the mixing and setting properties vis-a-vis 3M's P30. After looking at the composite being mixed, he immediately picked up a Centrix syringe, back-loaded it and found that it could be syringed into a prepared cavity on a typodont. He was favorably impressed by this syringable characteristic along with the property of controlled reactivity. He concurred that the material was condensable and that it knit to itself as he condensed it with an amalgam carrier. He then selected a flame-tipped, 12-fluted burr and ground the composite and the occlusal anatomy without galling the burr.

We then showed him a sample of an extracted second molar which had been bonded on one side with P10 and on the other side with Example 2 composite. No bonding preparation was made with either composite. He found, just as we had in previous trials, that the P10 could be flicked off the surface with the thumbnail whereas the Example 2 composite remained intact upon attempting to be debonded, even with a sharp-edged knife.

### Example 3

Another urethane composite was made with the following composition:

Part A:	Parts by weight
Liquidified diphenylmethane diisocyanate	35.2
Glyceryltriricinoleate	5.9
Amorphous glass 10 $\mu$ m (micron) average particle size	58.8
Fumed silica, untreated	1.5

Part B:	Parts by weight
6000 MW polyoxypropyleneoxide polyol triol	20.0
ethylenediamine tetrapropoxylate	14.0
sodiumaluminosilicate, 4 angstrom pore size	16.0
amorphous glass, 10 $\mu$ m (micron) average particle size	50.0

This system gave reactivity properties which suggested the following clinical parameters:

Clinical Parameters for class 1 restorations	Time required for each step	Total elapsed time
Mixing time	0.5 minutes	0.5 minutes
Back-filling syringe	0.5 minutes	1.0 minutes
Injecting composite into cavity	1.5 minutes	2.5 minutes
Waiting for cohesive body to build	1.0 minutes	3.5 minutes
Condensing the composite	1.0 minutes	4.5 minutes
Taking the bite articulation	0.5 minutes	5.0 minutes
Trimming off the excess composite	1.0 minutes	6.0 minutes
Grinding the occlusion to final articulation	2.0 minutes	8.0 minutes

An important attribute of the composites of the invention is that they can be mixed with variations encountered in actual clinical procedures yet give consistent and optimum restorative properties. One of the major conditions which can be varied in clinical procedures is the mix ratio. To test the mix ratio variability, several 12.7cm (5 inch) lines of Part A and Part B were laid out on a mixing pad. Five replicate tests gave weight ratios of Part A and Part B as follows: 1.4/1.3 grams, 1.2/0.8 grams; 1.0/1.0 grams; 1.1/1.2 grams; 1.0/1.0 grams. These ratio variations were translated to the following stoichiometric indices for the composite: 118, 163, 109, 100, and 109. These stoichiometric indices relate to the optimum theoretical properties of the composite. A stoichiometry of approximately 120 is considered to be the optimum stoichiometry for this composite system. Based upon these variations, it was considered that the composite should have reliable and level properties with variations in mixing almost to a 1.5:1 excess of Part A over Part B, and the converse- almost a 1.5:1 excess of Part B over Part A. The hardness properties of composite were tested at a later date and showed that the hardness did not vary significantly with ratios at a stoichiometry ranging from 70 to 160. Adding all of these extruded lines together in the above ratio tests

gave a composite ratio of 6.9 grams of Part A to 6.3 grams of Part B which relates to a 118 index, close to the theoretical optimum. These lines together gave a total weight of 13.2 grams of the system. Upon mixing, the system had the following reaction properties at 21°C (70 degrees F). ambient conditions: A syringing time of up to 2 minutes, a condensing period of between 2 and 4.5 minutes, an articulation bite time of  
 5 between 4.5 and 5.5 minutes, a carving time of between 5 and 7 minutes, and a grinding time of between 7 and 20 minutes. The composite continued to harden so that a hardness of 89 Shore D was achieved after 24 hours. The hardness did not change from 89 Shore D after 7 days on the benchtop at ambient conditions. The urethane had an excellent appearance and it had looked somewhat like tooth structure, although it was whiter and more opaque. The urethane composition was used to replace one class 1  
 10 amalgam restoration, a right maxillary second molar on experimental patient Number 1. The amalgam was removed leaving a very slight amount at the pulp base. The debris was thoroughly removed and the cavity dried. A calcium hydroxide base was applied and allowed to cure. The cavity was dried thoroughly. The urethane was mixed and back-loaded into a discardable-type syringe. The tapered tip was cut off slightly to provide approximately a one-sixteenth inch diameter opening in the syringe orifice. The urethane was  
 15 injected into the cavity and an excess applied. The urethane was applied at approximately 2 minutes after mixing.

### Claims

- 20 1. Method of forming restorative tooth structures, including mixing a first side comprising an isocyanato reagent under urethane polymer forming conditions simultaneously with a second side comprising a premix of both an hydroxylated tertiary amine reagent and a polyol reagent, shaping for use in a tooth restoration, and reacting to a polymeric urethane composition restorative tooth structure characterized in selecting as the polyol reagent a polyol forming a noncrystalline urethane polymer with said  
 25 isocyanato reagent under urethane polymer forming conditions, and selecting as the hydroxylated tertiary amine reagent an alkaryl amine, arylamine, mercaptan, alkylene oxide adduct of alkanol amines, alkoxyated or epoxyated ethylenediamines, triazines, amines and hydrazines having hydroxyl, thiol, or carboxyl functionality.
- 30 2. The method according to claim 1, including reacting said isocyanato reagent with said hydroxylated tertiary amine reagent to a crystalline urethane polymer, and with said polyol reagent to an amorphous polymer interdispersed with said crystalline polymer.
3. The method according to claim 1, including also employing as said second side per 100 parts by  
 35 weight from 10 to 30 parts of said polyol, from 10 to 30 parts of said hydroxylated tertiary amine, and the balance zeolite, silica, vitreous particulate, or mixtures thereof.
4. Compositions useful for restorative tooth structures, comprising a urethane polymer reaction product of  
 40 a first side comprising an isocyanato reagent reacted simultaneously with a second side comprising both a premix of an hydroxylated tertiary amine reagent and a polyol reagent characterized in which said polyol reagent is a polyol forming a noncrystalline urethane polymer with said isocyanato reagent under urethane polymer forming conditions.
- 45 5. The composition according to claim 4, in which said polyol is an hydroxyl-, thiol-, or carboxyl- poly-substituted oligomer having a molecular weight above about 500 and a segregated phase defining reaction with said isocyanato reagent relative to said amine reaction with said isocyanate reagent under the same urethane polymer forming conditions.
- 50 6. The compositions according to claim 5, in which said polyol reagent is a polytetraalkylenecoxide ether polyol or polyoxyalkylene ether polyol.
7. The composition according to claim 4, in which said polyol has a molecular weight above about 1000.
8. The composition according to claim 4, in which said isocyanato reagent comprises 4,4'-diphenyl-  
 55 methanediisocyanate.
9. The composition according to claim 4, in which tertiary amine reagent has a faster rate of reaction with said isocyanato reagent adduct than does said polyol reagent, whereby said urethane polymer

comprises a crystalline portion produced by reaction of said amine and said adduct and a noncrystalline portion produced by reaction of said polyol and said adduct, said crystalline portion being dispersed through said noncrystalline portion.

- 5 10. The composition according to claim 4, in which the urethane polymer obtained by reaction of said isocyanato reagent with said hydroxylated tertiary amine reagent is a crystalline urethane polymer, and the urethane polymer obtained by reaction of said isocyanato reagent with said polyol reagent is an amorphous polymer interdispersed with said crystalline polymer.
- 10 11. The composition according to claim 10, in which said polymer comprises per 200 parts by weight from 25 to 45 parts of 4,4'-diphenylmethane diisocyanate, from 3 to 8 parts of polytetramethyleneoxide ether polyol, D.B. castor oil, or glycerylricinoleate triester adducted with said 4,4'-diphenylmethane diisocyanate, from 0 to 30 parts of said polyol, from 10 to 60 parts of said hydroxylated tertiary amine, and the balance a hardening filler.
- 15 12. Natural tooth restoration structure, comprising in shaped conformance to a natural tooth, a urethane organic polymer according to claim 4  
having generally a glass transition temperature less than the temperature of the mouth environment.
- 20 13. A method of enhancing the malleability of a urethane polymer composition according to claim 4 to be shaped against a natural tooth, including incorporating an effective amount above about 5% by weight of zeolite in said composition with the proviso that treatment of the human or animal body according to Art. 52(4) EPC is excluded.
- 25 14. Method of preventing staining, wear, cracking or like degradation of acrylic dental composites which comprises overcoating said composite with a urethane polymer according to claim 4 in areas to be protected from degradation with the proviso that treatment of the human or animal body according to Art. 52(4) EPC is excluded.

#### 30 Revendications

- 35 1. Procédé de formation de structures de reconstitution dentaire, dans lequel on mélange un premier composant comprenant un corps réagissant du type isocyanate dans des conditions de formation de polyuréthane avec un second composant comprenant un prémélange d'un corps réagissant du type amine tertiaire hydroxylée et d'un corps réagissant du type polyol, on met en forme pour une utilisation dans une reconstitution dentaire et on fait réagir pour former une structure de reconstitution dentaire constituée d'une composition d'uréthane polymère, caractérisé en ce que l'on choisit comme corps réagissant du type polyol un polyol formant un polyuréthane non cristallin avec ledit corps réagissant du type isocyanate, et l'on choisit comme corps réagissant du type amine tertiaire hydroxylée une alkarylamine, une arylamine, un mercaptan, un produit d'addition d'oxyde d'alkylène sur des alcanolamines, des éthylènediamines alcoxylées ou époxydées, des triazines, amines ou hydrazines ayant une fonctionnalité hydroxyle, thiol ou carboxyle.
- 40 2. Procédé selon la revendication 1, dans lequel on fait réagir ledit corps réagissant du type isocyanate avec ledit corps réagissant du type amine tertiaire hydroxylée pour former un polyuréthane cristallin, et avec ledit corps réagissant du type polyol pour former un polymère amorphe entremêlé avec ledit polymère cristallin.
- 45 3. Procédé selon la revendication 1, dans lequel également on utilise comme second composant, pour 100 parties en poids, 10 à 30 parties dudit polyol, 10 à 30 parties de ladite amine tertiaire hydroxylée, et le reste de zéolite, silice, particules vitreuses ou mélanges de celles-ci.
- 50 4. Composition utile pour des structures de reconstitution dentaire, comprenant un polyuréthane formé comme produit réactionnel d'un premier composant comprenant un corps réagissant du type isocyanate ayant réagi avec un second composant comprenant un prémélange d'un corps réagissant du type amine tertiaire hydroxylée et d'un corps réagissant du type polyol, caractérisé en ce que ledit corps réagissant du type polyol est un polyol formant un polyuréthane non cristallin avec ledit corps

réagissant du type isocyanate dans les conditions de formation de polyuréthane.

- 5 5. Composition selon la revendication 4, dans laquelle ledit polyol est un oligomère polysubstitué par des groupes hydroxyle, thiol ou carboxyle ayant un poids moléculaire supérieur à 500 environ et une réaction définissant une phase séparée a lieu avec le corps réagissant du type isocyanate vis-a-vis de ladite réaction d'amine avec ledit corps réagissant du type isocyanate dans les mêmes conditions de formation de polyuréthane.
- 10 6. Composition selon la revendication 5, dans laquelle ledit corps réagissant du type polyol est un polyoxytétraalkylène-polyol ou un polyoxyalkylène-polyol.
7. Composition selon la revendication 4, dans laquelle ledit polyol a un poids moléculaire supérieur à 1000 environ.
- 15 8. Composition selon la revendication 4, dans laquelle ledit corps réagissant du type isocyanate comprend du 4,4'-diisocyanato-diphénylméthane.
- 20 9. Composition selon la revendication 4, dans laquelle le corps réagissant du type amine tertiaire réagit plus rapidement que le corps réagissant du type polyol avec le produit d'addition du corps réagissant du type isocyanate, si bien que ledit polyuréthane comprend une portion cristalline produite par réaction de ladite amine et dudit produit d'addition et une portion non cristalline produite par réaction dudit polyol et dudit produit d'addition, la portion cristalline étant dispersée dans la portion non cristalline.
- 25 10. Composition selon la revendication 4, dans laquelle le polyuréthane obtenu par réaction dudit corps réagissant du type isocyanate avec ledit corps réagissant du type amine tertiaire hydroxylée est un polyuréthane cristallin, et le polyuréthane obtenu par réaction dudit corps réagissant du type isocyanate avec ledit corps réagissant du type polyol est un polymère amorphe entremêlé avec ledit polymère cristallin.
- 30 11. Composition selon la revendication 10, dans laquelle ledit polymère comprend, pour 200 parties en poids, 25 à 45 parties de 4,4'-diisocyanato-diphénylméthane, 3 à 8 parties de polyoxytétraméthylène-polyol, d'huile de ricin D.B. ou de ricinoléate de glycéryle sous forme de produit d'addition avec le 4,4'-diisocyanato-diphénylméthane, 0 à 30 parties dudit polyol, 10 à 60 parties de ladite amine tertiaire hydroxylée et le reste d'une charge de durcissement.
- 35 12. Structure de reconstitution de dents naturelles, comprenant, sous une forme adaptée à une dent naturelle, un polyuréthane organique selon la revendication 4, ayant généralement une température de transition vitreuse inférieure à la température du milieu buccal.
- 40 13. Procédé pour améliorer la malléabilité d'une composition de polyuréthane selon la revendication 4 devant être mise en forme contre une dent naturelle, dans lequel on incorpore une quantité efficace supérieure à environ 5 % en poids de zéolite dans ladite composition, étant entendu qu'un traitement du corps humain ou animal est exclus conformément à l'article 52(4) de la CBE.
- 45 14. Procédé pour éviter une coloration, usure, fissuration ou dégradation analogue de composites dentaires acryliques, qui consiste à recouvrir ledit composite d'un polyuréthane selon la revendication 4 dans les zones à protéger contre une dégradation, étant entendu qu'un traitement du corps humain ou animal est exclus conformément à l'article 52(4) de la CBE.

#### Patentansprüche

- 55 1. Verfahren zur Herstellung von Zahnersatzstrukturen, wobei unter "Urethanpolymerisationsbedingungen eine erste Komponente, bestehend aus einem Isocyanatreagens, mit einer zweiten Komponente, bestehend aus einem Premix aus einem hydroxylierten tertiären Amin und einem Polyolreagens vermischt wird, die Mischung in eine für den Zahnersatz geeignete Form gebracht wird und zu einer Zahnersatzstruktur aus polymerem Urethan reagiert wird, dadurch gekennzeichnet, daß das Polyolreagens ein Polyol ist, welches ein nichtkristallines Urethanpolymer mit besagtem Isocyanatreagens

unter Urethanpolymerisationsbedingungen ergibt und das hydroxylierte tertiäre Amin ausgewählt wird aus Alkylaminen, Arylaminen, Mercaptan, Alkylenoxidaddukten von Alkanolaminen, alkoxylierten oder oxylierten Ethylendiaminen, Triazinen, Aminen und Hydrazinen mit Hydroxyl, Thiol- oder Carbonylfunktionen.

- 5 2. Verfahren gemäß Anspruch 1, wobei besagtes Isozyanatereagenz mit dem hydroxylierten tertiären Aminreagenz zu einem kristallinen Urethanpolymer umgesetzt wird und das Polyolreagenz zu einem amorphen Polymer reagiert, welches in dem kristallinen Polymer dispergiert ist.
- 10 3. Verfahren gemäß Anspruch 1, wobei als zweite Komponente eine solche verwendet wird, die auf 100 Gewichtsteile 10 - 30 Teile des Polyols und 10 - 30 Teile des hydroxylierten tertiären Amins enthält und der Rest aus Zeolit, Silikat, glasigen Partikeln oder Mischungen davon, besteht.
- 15 4. Mischung, die zur Herstellung von Zahnersatzstrukturen geeignet ist, bestehend aus einem Urethanpolymer- Reaktionsprodukt einer ersten Komponente, bestehend aus einem Isocyanatereagenz und einer zweiten Komponente, welche ein Premix aus einem hydroxylierten tertiären Aminreagenz und ein Polyolreagenz enthält, **dadurch gekennzeichnet**, daß das Polyolreagenz ein Polyol ist, welches ein nichtkristallines Urethanpolymer mit dem Isocyanatereagenz unter Urethanpolymer bildenden Bedingungen bildet.
- 20 5. Mischung gemäß Anspruch 4, in welcher das Polyol ein Hydroxyl-, Thiol- oder Carboxyl-polysubstituiertes Oligomer ist, welches ein Molekulargewicht über ungefähr 500 hat und eine abgetrennte Phase bildende Reaktion mit dem Isocyanatereagenz, bezogen auf die Aminreaktion mit dem Isocyanatereagenz unter den gleichen Urethanpolymer bildenden Bedingungen, definiert.
- 25 6. Mischung gemäß Anspruch 5, in welchem das Polyolreagenz ein Polytetraalkylenoxidetherpolyol oder Polyoxyalkylenetherpolyol ist.
- 30 7. Mischung gemäß Anspruch 4, in welchem das Polyol ein Molekulargewicht von ungefähr 1000 hat.
8. Mischung gemäß Anspruch 4, in welchem das Isocyanatereagenz 4,4'-Diphenylmethandiisocyanat ist.
- 35 9. Die Mischung gemäß Anspruch 4, in welchem das tertiäre Aminreagenz eine schnellere Reaktionsrate mit dem Isocyanatereagenzaddukt aufweist als das Polyolreagenz, wobei das Urethanpolymer aus einem kristallinen Teil besteht, welcher durch die Reaktionen des Amins mit dem Addukt entstanden ist und einen nichtkristallinen Teil aufweist, der durch Reaktion von dem Polyol mit dem Addukt entstanden ist; wobei der kristalline Teil in dem nichtkristallinen Teil dispergiert ist.
- 40 10. Die Mischung gemäß Anspruch 4, in dem das Urethanpolymer, welches durch Reaktion des Isocyanatereagenzes mit dem hydroxylierten tertiären Aminreagenz entstanden ist, ein kristallines Urethanpolymer ist, und das Urethanpolymer, welches durch Reaktion des Isocyanatereagenzes mit dem Polyolreagenz erhalten wird, ein amorphes Polymer ist, welches in dem kristallinen Polymer dispergiert ist.
- 45 11. Die Mischung gemäß Anspruch 10, in welcher das Polymer auf 200 Gew.-Teile aus 25 - 45 Teilen 4,4'-Diphenylmethandiisocyanat, 3 - 8 Teilen Polytetramethylenoxydetherpolyol, Rizinusöl oder Glycerinrizinusoleattriester-addukt mit besagtem 4,4'-Diphenylmethandiisocyanat, 0 - 30 Teilen des Polyols und 10 - 60 Teile des hydroxylierten tertiären Amins besteht und der Rest ein härtender Füllstoff ist.
- 50 12. Natürliche Zahnersatzstruktur, geformt übereinstimmend mit einem natürlichen Zahn, bestehend aus einem organischen Urethanpolymer gemäß Anspruch 4, welches eine Glasübergangstemperatur aufweist, die unterhalb der Temperatur der Umgebung des Mundes liegt.
- 55 13. Verfahren zur Verstärkung der Verformbarkeit von Urethanpolymermischungen gemäß Anspruch 4 zur Formung wie natürliche Zähne, **dadurch gekennzeichnet**, daß eine wirksame Menge von mehr als ungefähr 5 Gew.-% Zeolit in die Mischung eingearbeitet ist, wobei eine Behandlung des menschlichen oder tierischen Körpers gemäß Art. 52 (4) EPÜ ausgeschlossen ist.

14. Verfahren zum Verhindern von Fleckigwerden, Abnutzung, Brüchen oder ähnlichem Abbau von Acryl-  
dentalmischungen, dadurch gekennzeichnet, daß die Mischung mit einem Überzug aus einem  
Urethanpolymer gemäß Anspruch 4 in den vor Abbau zu schützenden Gebieten versehen wird, mit  
dem Vorbehalt, daß eine Behandlung des menschlichen oder tierischen Körpers gemäß Art. 52 (4)EPÜ  
ausgeschlossen ist.

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